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Process for the Preparation of Synthesis Gas

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Description of the Invention

The invention concerns a process for the preparation of synthesis gas by parallel steam reforming of a hydrocarbon
5 containing feedstock in a autothermal reformer (ATR) and in a series of adiabatic steam reformers with addition of carbon monoxide rich gas to the feedstock.

Background of the Invention

10

A plant for production of synthetic diesel and other synthetic hydrocarbons consists of three main parts. In the first main unit synthesis gas (a mixture of hydrogen and carbon oxides) is produced from the feedstock which is usually natural gas or a similar light hydrocarbon feedstock.
15 In the second main unit, the actual hydrocarbon synthesis takes place usually by the Fischer-Tropsch synthesis. In the final part often known as the Product Workup unit (PWU) the raw products are refined and/or separated to give the desired end products. The present invention relates to an
20 improved method for production of synthesis gas.

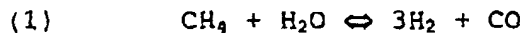
Today, one of the most cost effective and efficient methods for production of synthesis gas is by Autothermal Reforming (ATR). In ATR the light hydrocarbon feedstock with addition
25 of steam reacts with a sub-stoichiometric amount of oxygen to produce synthesis gas. An ATR reactor consists of a burner, a combustion chamber, and a catalyst bed in a refractory lined pressure shell.

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For the Fischer-Tropsch synthesis to be as effective as possible, a specific synthesis gas composition is often de-

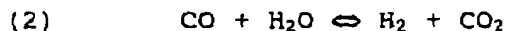
sired. In many cases the desired synthesis gas composition is given by the ratio of the content of hydrogen to the content of carbon monoxide. The desired ratio is often approximately 2.0. With most operating conditions ATR is not
5 able to produce this ratio. Instead a carbon dioxide containing stream must be recirculated to a location upstream the ATR reactor. This recirculation stream is often a tail gas, which is essentially a by-product from the Fischer-Tropsch synthesis unit and/or the Product Work-up unit.
10 The main components in the tail gas are carbon monoxide, carbon dioxide, hydrogen and various light hydrocarbons such as methane, ethane, propane, ethylene and propylene. Synthesis gas production may account for more than 50% of the total capital cost in a Fischer-Tropsch plant. For a
15 plant based on ATR a large fraction of the cost of the synthesis gas production unit arises from the air separation unit needed to produce oxygen. Hence, there is a considerable interest in methods for reducing the oxygen consumption per unit of synthesis gas produced.
20
The installation of a heat exchange steam reforming unit (HESRU) in parallel with the ATR is one method for increasing the synthesis gas production without the corresponding need for a larger air separation unit. In this case the
25 feed (typically a mixture of desulphurised natural gas and steam or a pre-reformed mixture) is split between the ATR and the HESRU. The tail gas is added either to the ATR feed stream, the HESRU feed stream or to both feed streams. The effluents from the ATR and the HESRU are combined to give
30 the synthesis gas, which is sent to the Fischer-Tropsch synthesis section.

In the HESRU the endothermic steam reforming reaction of the hydrocarbons take place as illustrated below, using methane as an example:



5

The steam reforming reactions are accompanied by the water gas shift reaction:



10 The above two reactions are close to equilibrium at the HESRU outlet. The temperature of the exit gas is above 800°C to ensure a satisfactory methane conversion. The amount of tail gas added is adjusted to give the desired exit gas composition. Typically, the installation of the
15 HESRU will increase the amount of tail gas recirculated to the process.

As described above, the HESRU reduces the oxygen consumption. However, the HESRU itself may be quite cost intensive
20 and methods for reducing the size are desired. The catalyst in steam reforming units is often nickel supported on ceramic carriers such as alumina.

Steam reforming involves the risk of detrimental carbon
25 formation on the catalyst such as (example for methane):



Detrimental carbon formation on the catalyst may result in catalyst breakage, catalyst deactivation, and will eventually
30 block the flow passage and should be avoided. One method known in the art to avoid carbon formation is to add a sufficient amount of steam to the hydrocarbon process

stream. However, in Fischer-Tropsch plants it is in general desirable to minimise the amount of steam added to the feedstock. One method for reducing the required amount of steam without carbon formation is to use noble metal catalysts (Rostrup-Nielsen et al., J. of Catalysis 144, pages 38-49, 1993). However, the cost of noble metals as compared to nickel is very high and considering the size of the HESRU it is desirable to reduce the amount of catalyst.

10 The invention is a process for the production of synthesis gas by catalytic steam reforming of a hydrocarbon containing feedstock in parallel in an autothermal steam reformer and in at least two adiabatic steam reformers in series wherein the feedstock to the at least two adiabatic steam reformers is preheated by indirect heat exchange with a steam reformed effluent stream from the autothermal steam reformer and a steam reformed effluent stream from the at least one adiabatic steam reformer and wherein carbon monoxide containing gas is added to the feedstock prior to the steam reforming in the autothermal steam reformer and/or prior to the steam reforming in at least one of the at least two adiabatic steam reformers, the carbon monoxide containing gas is added in an amount resulting in a product stream in which the ratio of the amount of hydrogen to the amount of carbon monoxide is between 1.8 and 2.3.

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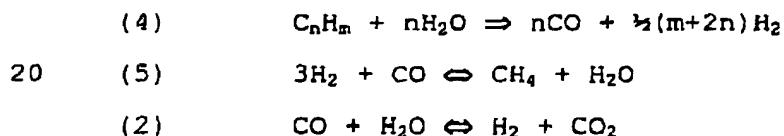
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30 The above aspects and features are disclosed in greater detail in the following description by reference to the drawings in which Fig. 1 shows a specific embodiment of the invention.

A hydrocarbon containing feed stream 1 is divided into a feed stream 3 for the ATR and a feed stream 2 for the adiabatic reformers 8. Optionally, stream 3 can be pre-reformed and/or further heated (not shown in Fig. 1). The pre-reforming is in this case carried out by an adiabatic pre-reformer as described in the art (e.g. Christensen, Appl.Cat. A 138, page 285, 1996)

The stream 3 is optionally mixed with a tail gas 4 resulting in a feed stream 6 for the ATR 7. Oxidant 5 either in the form of air or oxygen or mixtures thereof is fed to the ATR 7 in which synthesis gas is produced and withdrawn through line 8.

Tail gas 9 is optionally added to the feed stream 2 resulting in feed stream 37 for adiabatic reactor 10. In adiabatic reactor 10, steam reforming, methanation and shift reactions occur as follows:



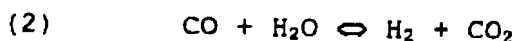
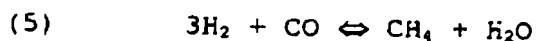
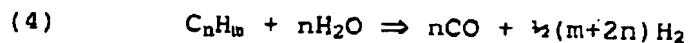
Product gas 20 is withdrawn from reactor 10. Gas stream 20 is subjected to a series of identical and sequential steps as follows:

Addition of tail gas 11 resulting in a mixed stream 21.

Increasing the temperature of stream 21 in heat exchanger 13 resulting in stream 22.

Optional addition of tail gas 12 resulting in mixed stream 23.

5 Processing of stream 23 in adiabatic reactor 14 in which the following reactions occur:



10 Withdrawing the product from adiabatic reactor 14 in stream 24.

15 The number of steps is adjusted until a predetermined gas composition and temperature is reached. The product stream 24 from the final adiabatic reactor 14 is mixed with the product stream 8 from the ATR resulting in synthesis gas stream 32. The synthesis gas 32 is cooled in one or several heat exchangers 13 providing the heat for the increase in temperature of stream(s) 21 as described above. The cooled stream 36 is the product synthesis gas.

25 In another embodiment of the invention the duty for the heating of process stream(s) 21 may partially or completely be obtained from other streams in the Fischer-Tropsch complex. This depends upon the optimal heat integration in the given plant.

30 The total amount of tail gas added in stream 4, 9, 11, and 12 is adjusted to give the desired product synthesis gas composition typically with a hydrogen to carbon monoxide ratio between 1.8 and 2.3.

The catalyst in reactor 10 and in reactor(s) 14 may be either in form of pellets or more preferably in the form of catalysed hardware. The catalytic coating of a metal surface (wash coating) is a well known process (a description is given in e.g. Cybulski, A., and Moulijn, J. A., Structured catalysts and reactors, Marcel Dekker, Inc, New York, 1998, Chapter 3, and references herein). The appropriate material, preferable a ferritic steel containing Cr and/or Al, is heated to a temperature preferably above 800°C in order to form a layer of Cr and/or Al oxide. This layer facilitates a good adhesion of the ceramic to the steel. A thin layer of a slurry containing the ceramic precursor is applied on the surface by means of e.g. spraying, painting or dipping. After applying the coat the slurry is dried and calcined at a temperature usually in the region 350-1000°C. Finally the ceramic layer is impregnated with the catalytic active material. Alternatively the catalytic active material is applied simultaneously with the ceramic precursor. This can in the present invention either be directly to a channel wall in which the process gas flows or attached to a metallic element. In the latter case the metallic elements can be placed in the channel in which the process gas flows. The metallic element may be either in form of a monolith or cross-corrugated structures. Further catalyst hardware is in form of catalyst being deposited in metallic or ceramic structure, which is adhered to wall of the reactor. Structured catalysts in the form of ceramic or metallic monoliths or cross-corrugated ceramic or metallic structures may also be used. The catalytic material itself may be either nickel or noble metals (Pt, Pd, Ru, Rh, Ir) or mixtures thereof.

The advantages of the process shown in Fig. 1 are several. The heat transfer and the chemical reactions are decoupled making it possible to optimise both individually. In addition the change of catalyst is easier than with an integrated apparatus. The fact that several reactors are employed means that the catalyst can be tailored more specifically to the given operating conditions. As an example of this nickel based catalysts could be used at the relative low temperatures while noble metals can be used at higher temperatures to avoid carbon formation.

The use of several heat exchangers may facilitate the use of materials tailored to the operating conditions. Specifically, the choice of materials may be adjusted to the temperature in each exchanger. Also, metal dusting corrosion must be considered at these operating conditions. In some of the heat exchangers the risk of metal dusting is more pronounced than in others. In these exchangers materials with high resistance to metal dusting should be applied, while this may not be necessary in other cases.

The use of several locations to inject tail gas into the process gas streams has the advantage that the risk of carbon formation on the catalyst is reduced. Carbon formation may occur from higher hydrocarbons (hydrocarbon compounds with 2 or more carbon atoms) according to the following reaction:



Especially olefins may even in small concentration be the cause for detrimental carbon formation on the catalyst. It is known that increasing the hydrogen-to-olefin ratio has a

positive effect on avoiding carbon formation. With a split of the tail gas the hydrogen-to-olefin ratio increases at the inlet to each of the adiabatic reactors because no olefins are present in the feed gas stream 1.

CLAIMS

1. Process for the production of synthesis gas by catalytic steam reforming of a hydrocarbon containing feedstock in parallel in an autothermal steam reformer and in at least two adiabatic steam reformers in series wherein the feedstock to the at least two adiabatic steam reformers is preheated by indirect heat exchange with a steam reformed effluent stream from the autothermal steam reformer and a steam reformed effluent stream from the at least one adiabatic steam reformer and wherein carbon monoxide containing gas is added to the feedstock prior to the steam reforming in the autothermal steam reformer and/or prior to the steam reforming in at least one of the at least two adiabatic steam reformers, the carbon monoxide containing gas is added in an amount resulting in a product stream in which the ratio of the amount of hydrogen to the amount of carbon monoxide is between about 1.8 and 2.3.
2. Process according to claim 1, wherein catalyst in at least one of the adiabatic steam reformers is in form of pellets.
3. Process according to claim 1, wherein catalysts in at least one of the adiabatic steam reformers is in form of catalysed hardware.
4. Process according to claim 3, wherein the catalysed hardware is arranged on structured metallic or ceramic elements or on monoliths.

5. Process according to claims 1, wherein active material of a catalyst in a first of the adiabatic steam reformers is nickel and the active material in a last of the adiabatic steam reformers is a noble metal or a mixture of noble metals.

6. Process according to claims 1, wherein the preheating is combined with catalytic steam reforming between at least one of the adiabatic steam reformers.

7. Process according to claims 1, wherein an oxidant to the autothermal steam reformer contains at least 90% oxygen by volume.

8. Process according to claims 1, wherein the hydrocarbon containing feedstock is a mixture of natural gas, steam and hydrogen.

9. Process according to claim 1, wherein the hydrocarbon containing feedstock is pre-reformed natural gas.

10. Process according to any one of the preceding claims, wherein the carbon monoxide containing gas is tail-gas from a Fischer-Tropsch process.

ABSTRACT

Process for the production of synthesis gas by catalytic steam reforming of a hydrocarbon containing feedstock in parallel in an autothermal steam reformer and in at least two adiabatic steam reformers in series wherein the feedstock to the at least two adiabatic steam reformers is preheated by indirect heat exchange with a steam reformed effluent stream from the autothermal steam reformer and a steam reformed effluent stream from the at least one adiabatic steam reformer and wherein carbon monoxide containing gas is added to the feedstock prior to the steam reforming in the autothermal steam reformer and/or prior to the steam reforming in at least one of the at least two adiabatic steam reformers, the carbon monoxide containing gas is added in an amount resulting in a product stream in which the ratio of the amount of hydrogen to the amount of carbon monoxide is between about 1.8 and 2.3.

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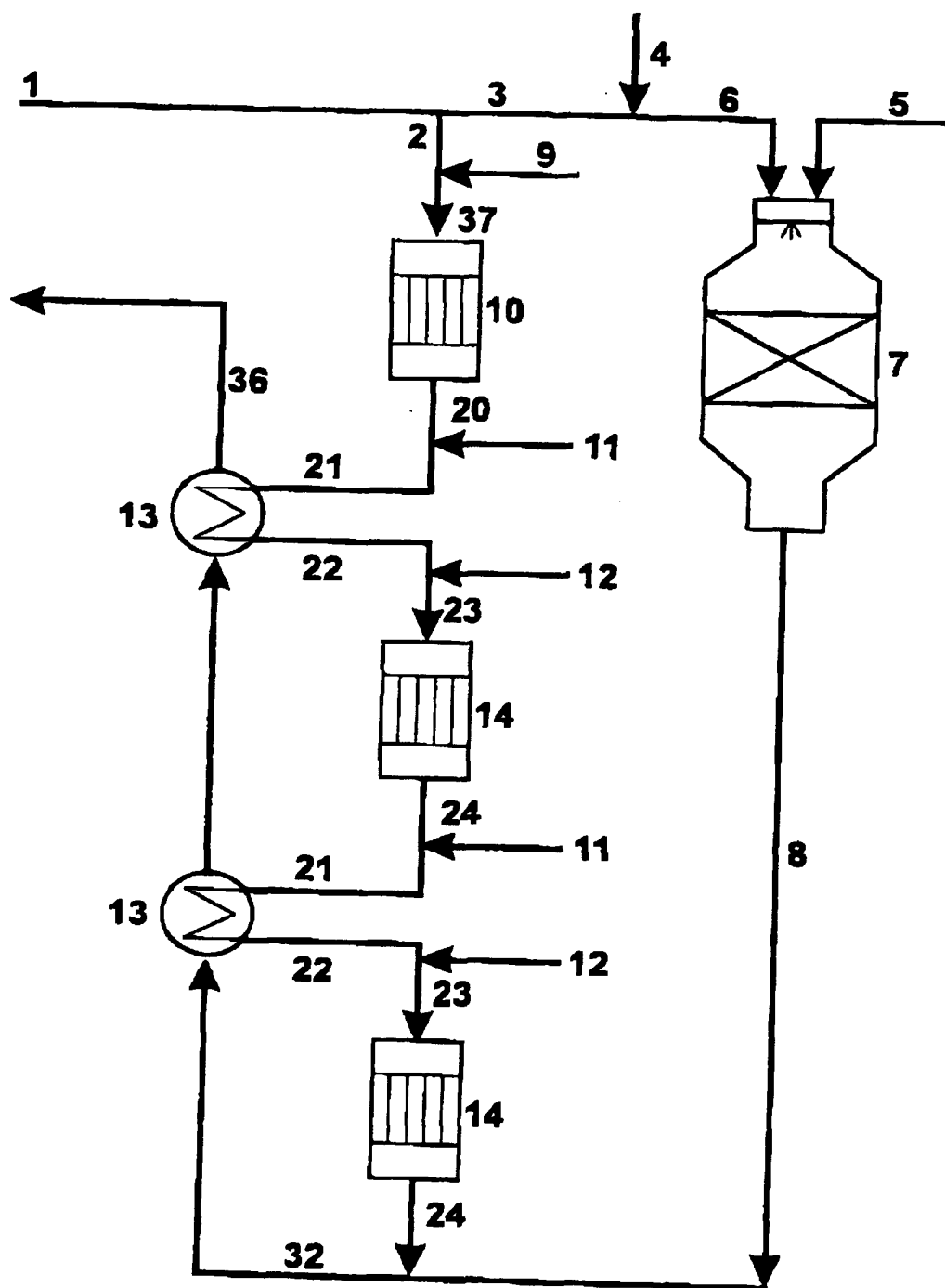


Fig. 1